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(54) TRANSPARENT CONDUCTIVE FILM AND DISPLAY DEVICE

(57)Abstract:
PROBLEM TO BE SOLVED: To improve the visible ray average transmittance of a film and to obtain electromagnetic wave shielding effect and electrification preventing effect by providing a conductive layer that is formed by applying a paint, where the chain-shaped aggregate of a metal fine particle is dispersed.
SOLUTION: In the chain-shaped aggregate of metal fine particles, a plurality of meal fine particles are connected in a chain, and the average length of the chain is preferably in the range 5 nm-200 nm is terms of conductivity and transparency. By applying a paint containing the chain-shaped aggregate onto a base and baking it after drying for forming a film, the contact electrical resistance between particles can be minimized, thus obtaining high conductivity, regardless of whether the conductive layer is a thin film and hence obtaining a transparent conductive film that has not only improved electrification preventing effect/electromagnetic shielding effect but also high transparency.

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] A transparence electric conduction film characterized by having a conductive layer which applied a coating which chain-like floc of a metal particle distributed, and was formed.
[Claim 2] A transparence electric conduction film according to claim 1 characterized by being within the limits whose average length of said chain-like floc is 5nm - 200nm.
[Claim 3] A transparence electric conduction film according to claim 1 or 2 characterized by carrying out the laminating of the clear layer of at least one layer from which said conductive layer and refractive index differ to the upper layer and/or a lower layer of said conductive layer.
[Claim 4] A display characterized by coming to form a transparence electric conduction film according to claim 1 to 3 in the screen.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] This invention has the antistatic effect and electromagnetic wave shielding effect which used and were especially excellent in the screens, such as a cathode-ray tube and a plasma display, about the indicating equipment with which a transparence electric conduction film and this transparence electric conduction film were formed in the screen, and its membranous light average transmission coefficient is high, and its hue of a transparency image is natural, and it relates to the indicating equipment which formed the transparence electric conduction film excellent also in endurance, such as salt water resistance, oxidation resistance, and ultraviolet resistance, and this transparence electric conduction film in the screen.
[0002]
[Description of the Prior Art] Since an alphabetic character and an image are projected on the screen by making an electron beam bombardment [red and the phosphor screen which emits light green and blue], dust adheres with static electricity generated in this screen, visibility falls, and also the cathode-ray tube which is one sort of the indicating equipment used as TV Braun tube, a display of a computer, etc. has **** which radiates an electromagnetic wave and affects environment. Moreover, also in the plasma display with which application as a flat TV etc. is advanced, the possibility of generating of static electricity or electromagnetic wave radiation is pointed out recently.
[0003] In order to solve these problems, what becomes JP,8-77832,A from the transparence metal thin film by the metal particle of within the limits with a mean particle diameter of 2nm - 200nm which contains silver at least, and the transparence thin film with which this differs from a refractive index as a transparence electric conduction film excellent in the electromagnetic wave shielding effect and the acid-resisting effect is proposed.
[0004]
[Problem(s) to be Solved by the Invention] However, these transparence metal thin films are not necessarily enough as conductivity, and absorption arises in the 400nm - 500nm transmitted light depending on a silver light transmission spectrum. The problem that an electric conduction film colors it yellow and the hue of a transparency image changes unnaturally, Since the surface electrical resistance of an electric conduction film will go up and an electromagnetic wave shielding effect will fall if it will be immersed three days or more into the problem that the nonuniformity of the transparency color resulting from thickness distribution tends to be conspicuous, and salt water, since the membranous light average transmission coefficient is low Problems, like use in the location which is easy to be influenced of ****, such as the seashore, takes cautions were not solved. The transparence electric conduction film which was made in order that this invention might solve the above-mentioned technical problem, therefore whose membranous light average transmission coefficient was [that purpose] high, was excellent in the conductivity which brings about the electromagnetic wave shielding effect **** antistatic effect, and was excellent also in the endurance which the hue of a transparency image is natural and is represented by salt water resistance, and this transparence electric conduction film are in offering the display formed in the screen.
[0005]
[Means for Solving the Problem] In order to solve the above-mentioned technical problem, this invention offers a transparence electric conduction film which has a conductive layer which applied a coating which chain-like floc of a metal particle distributed, and was formed in claim 1. As for chain-like floc, two or more metal particles mean the shape of a straight chain, and floc which it comes to connect branched-chain or annularly here. As for the average length of chain-like floc, in the above, it is desirable that it is within the limits of 5nm - 200nm. In the above, it is desirable that the laminating of the clear layer of at least one layer from which said conductive layer and refractive index differ is carried out to the upper layer and/or a lower layer of a conductive layer. In claim 4, as for this invention, one of the aforementioned transparence electric conduction films provides the screen with formation, now a becoming display again.
[0006]
[Embodiment of the Invention] Hereafter, a desirable example explains the gestalt of operation of this invention. That this invention persons should give visibility and an electromagnetic wave shielding effect excellent in the screen of a display If a transparence electric conduction film is formed using the coating which the chain-like floc of the result of research, especially a metal particle distributed wholeheartedly about the transparence electric conduction film formed by applying the coating containing a metal particle The metal particle acquired the knowledge that the transparence electric conduction film which has the conductive ability which was more transparent than the case where independent distribution is being carried

out to homogeneity, and was moreover excellent in it could be created, and reached this invention.
[0007] Hereafter, this invention is explained in more detail. For the conductive layer of the transparence electric conduction film of this invention, although the chain-like floc of a metal particle is formed using the coating for conductive layer formation distributed to homogeneity as a whole and thickness is a thin film of 10nm - 30nm, a surface-electrical-resistance value is 1x105. The high conductivity below omega/** is held, and the average transmission coefficient of the light has the high light transmission nature of 80% or more. By baking, after the chain-like floc of a conductive particle has become entangled with the detailed network structure although the reason the aforementioned conductive layer is equipped with high conductivity and high light transmission nature is not necessarily clear It is thought by forming a far good electric conduction path by the small particulate number, and forming the crevice between meshes greatly compared with the homogeneity dispersion layer of an independent distribution particle etc. compared with the dispersion layer which the contact electricity resistance condensed a large independent distribution particle, and the shape of massive and an island, that the permeability of light also improves.
[0008] As for the particle size of each metal particle which forms the chain-like floc of a metal particle in the above, it is desirable that it is within the limits of 1nm - 10nm. Since the property as a metal is spoiled as the particle size of each metal particle is less than 1nm, and conductivity falls, it is not desirable, and if it exceeds 10nm, since chain-like floc will not be obtained but it will become easy to generate the floc of the shape of massive or an island, it is not desirable.
[0009] As a metal particle used here, noble-metals particles, such as gold, silver, palladium, a ruthenium, platinum, a rhodium, iridium, and an osmium, are effective. The rate of an excellent article in the membrane formation production process which could obtain the chemical stability represented by the electric-field electric shielding nature in which especially gold was excellent, without disturbing the hue of a transparency image when the light transmission engine performance and conductive ability were high and this was applied to the screen of a display, and salt water resistance, the thickness nonuniformity of a paint film stopped being able to be conspicuous easily since the light transmission engine performance was still higher, and has especially so far been regarded as questionable is improved sharply. Moreover, in addition to this golden particle, other metals, for example, silver, copper, platinum, palladium, a ruthenium, a rhodium, iridium, the rhenium, the osmium, etc. may be included. It is cheaply [comparatively easily as colloid dispersion liquid anc] available, and since conductivity is highly excellent in antistatic nature and electromagnetic wave electric shielding nature, especially silver is effective [maintaining conductivity] to reduce the cost of a transparence electric conduction film further. When silver is independently used as electric conduction material, since salt water resistance is bad, there is no endurance, but if gold is used as mixture used as the principal component, chemical stability will increase and practically sufficient endurance will be acquired.
[0010] two or more metal particles connect the chain-like floc of a metal particle in the shape of a chain, for example, it is typically illustrated to drawing 1 -- as -- the shape of a straight chain (1), and branched-chain -- (2) and annular -- any are sufficient as (3) or those gestalten (4) that were compounded. The average length of the chain has a still more preferably desirable thing within the limits of 10nm - 100nm from a viewpoint of conductivity and transparency within the limits of 5nm - 200nm. By less than 5nm, the electric resistance between particles becomes [the average length of chain-like floc] large, and sufficient conductivity may not be acquired. Moreover, if average length exceeds 200nm, whenever [light-scattering] increases and the transparency of a paint film may be spoiled.
[0011] If the coating containing this chain-like floc is applied on a base material and membranes are baked and formed after desiccation at the temperature within the limits of 100 degrees C - 1000 degrees C Although the contact electricity resistance between particles is suppressed small and a conductive layer is a thin film of 10nm - 30nm, the surface-electrical-resistance value is 1x105. The high conductivity below omega/** is acquired. The transparence electric conduction film with which the antistatic effect and the electromagnetic wave shielding effect are not only excellent as the result, but the thickness nonuniformity which a light average transmission coefficient combines also with the high transparency of 80% or more cannot be easily conspicuous is obtained.
[0012] There are various methods as the formation method of the chain-like floc of a metal particle. For example, in case the metal hydrosol is made to generate, the aqueous solution of a metal salt is adjusted to pH 5-7, and the method of adding the reducing agent of the mol equivalent 0.5 to 3 times to the metal ion in this solution etc. is mentioned. When pH of a metal salt water solution is larger than 7, grain growth of the metal particle itself progresses to place ** with more reducing agents than the 3 time mol equivalent too much, and precipitate arises in it. Moreover, when pH of a metal salt water solution is smaller than 5, or when there are few reducing agents than the 0.5 time mol equivalent, an independent distribution particle generates, or a reduction reaction does not fully advance and a metal particle does not generate.
[0013] As other formation methods of the chain-like floc of a metal particle, there are a method of holding metal particle dispersion liquid for several hour - number 10 hours to the temperature below the boiling poin of about 40 degrees C - a dispersion medium, the method of adding organic compounds, such as alcohol, and controlling the polarity of a dispersion medium, etc. Since the optimum conditions for formation of chain-like floc change with classes of metal particle even if it is which method, it is necessary to search for optimum conditions suitably by preliminary experiment.
[0014] As for the aforementioned conductive layer, in addition to the chain-like floc of the aforementioned metal particle, in the transparence electric conduction film of this invention, mean particle diameter may contain the silica particle 100nm or less to the aforementioned metal particle chain-like floc by 1 % of the weight - 60% of the weight of within the limits. Film reinforcement of the conductive layer which applied said coating for conductive layer formation containing a silica particle, and formed membranes improves

remarkably, and its scratch reinforcement improves. Moreover, when preparing one or more layers of clear layers which have a refractive index which is different from the refractive index of this conductive layer in that upper layer and/or lower layer by making a conductive layer contain a silica particle, since wettability with the silica system binder component of a clear layer is good, there is also an advantage whose adhesion of both layers improves, and scratch reinforcement can be improved further. As for a silica particle, it is still more desirable to make it contain to metal particle chain-like floc from a viewpoint which reconciles improvement in film reinforcement and conductivity by 20 % of the weight - 40% of the weight of within the limits.

[0015] If the aforementioned conductive layer is required, film reinforcement and for the purpose of conductive improvement besides the aforementioned component Moreover, other components, For example, silicon, aluminum, a zirconium, a cerium, titanium, an yttrium, Oxides, such as zinc, magnesium, an indium, tin, antimony, and a gallium, The particle of the inorganic substance which uses a multiple oxide or a nitride especially the oxide of an indium or tin, double ********, or a nitride as a principal component, Polyester resin, acrylic resin, an epoxy resin, melamine resin, urethane resin, Organic, inorganic system binder components, etc., such as hydrolyzate of metal alkoxides, such as organic system synthetic resin, such as butyral resin and ultraviolet-rays hardening resin, silicon, titanium, and a zirconium, or a silicone monomer, and silicone oligomer, may be included.

[0016] In order to apply the coating for conductive layer formation containing the aforementioned metal particle chain-like floc on a base material, each usual thin film coating technology, such as a spin coat method, the roll coat method, a spray method, the bar coat method, a dip method, the meniscus coat method, and gravure, is usable. Among this, since a spin coat method can form the thin film of uniform thickness in a short time, it is the especially desirable applying method. A paint film is dried after spreading and a conductive layer is formed on the surface of a base material by baking at 100 degrees C - 1000 degrees C.

[0017] The conductive ability of a transparence electric conduction film required in order to demonstrate an electromagnetic wave shielding effect in addition to the antistatic effect is expressed by the following formula 1.

S=50+10 log(1/rhof)+1.7troot (f/rho) -- The inside of formula 1 type, S (dB) ; An electromagnetic wave shielding effect, rho (ohm-cm); the volume resistivity of a conductive layer, f (MHz) ; electromagnetic wave frequency, t (cm) ; It is the thickness of a conductive layer. Since it is desirable to consider as below 1-micrometer (1x10 to 4 cm) degree from a viewpoint of light transmittance, Thickness t can express the electromagnetic wave shielding effect S with the following formula 2 in approximation here, if the term which contains Thickness t in a formula 1 is disregarded.

S=50+10 log (1/rhof) the -- type 2 — here, the electromagnetic wave shielding effect of S (dB) is so large that a value is large.

[0018] general -- an electromagnetic wave shielding effect — S> 30dB — be -- if it is ** validity and further S>60dB, it will be considered that it is superior. Moreover, generally the frequency of the electromagnetic wave used as the target for regulation is 10kHz - 1000MHz. Since it considers as within the limits, as conductivity of a transparence electric conduction film, it is 103. Omega-cm The following volume resistivity values (rho) are needed. That is, the one where the volume resistivity value (rho) of a transparence electric conduction film is lower can cover the electromagnetic wave of more extensive frequency effectively. In order to fulfill this condition, it is desirable for the thickness of the conductive layer in a transparence electric conduction film to set to 10nm or more, and to make the further aforementioned metal particle contain 10% of the weight or more. When the thickness of a conductive layer is [the content of 10nm Suemitsu or a metal particle] less than 10 % of the weight, conductivity falls, and it becomes difficult to acquire a substantial electromagnetic wave shielding effect.

[0019] As for the transparence electric conduction film of this invention, it is desirable to come to carry out the laminating of the clear layer of at least one layer to the aforementioned upper layer and/or the aforementioned lower layer of a conductive layer. As for this clear layer, it is desirable that it is what has the refractive index of the aforementioned conductive layer and a different refractive index. It not only protects a conductive layer, but by this, it can remove or mitigate effectively the outdoor daylight reflection in the interface between layers of the obtained transparence electric conduction film.

[0020] As a material which forms a clear layer, hydrolyzate, a silicone monomer, or silicone oligomer of metal alkoxides, such as the thermoplasticity of polyester resin, acrylic resin, an epoxy resin, butyral resin, etc., a thermosetting property or light and electron ray hardenability resin, silicon, aluminum, titanium, and a zirconium, etc. is independent, for example, or it is mixed and used.

[0021] Membranous surface hardness is high and especially a desirable clear layer is SiO2 with a comparatively low refractive index. It is a thin film. this SiO2 as the example of the material which can form a thin film -- for example, a degree type -- the mixture beyond one sort or it of the compound expressed with M(OR) mRn (M is Si among a formula, R is the alkyl group of C1-C4, m is the integer of 1-4, and n is the integer of 0-3, and m+n is 4) or its partial hydrolysate can be mentioned. As an example of the compound of said formula, it is especially a tetra-ethoxy silane (Si4 (OC2H5)). It is suitably used from a viewpoint of thin film organization potency, transparency, cementation nature with a conductive layer, film reinforcement, and acid resistibility ability.

[0022] As long as it can set the aforementioned clear layer as a different refractive index from a conductive layer, it may contain precursors which can generate these by printing, such as various resin, a metallic oxide, a multiple oxide, or a nitride.

[0023] Formation of a clear layer can be performed by the method of applying the spreading liquid (coating

[redacted]

"reducing agent" with (titanium metal equivalent)

for clear layer formation) containing the aforementioned component to homogeneity like the method used for formation of a conductive layer, and forming membranes. Each usual thin film spreading technology of spreading, such as a spin coat method, the roll coat method, a spray method, the bar coat method, a dip method, the meniscus coat method, and gravure, is usable. Among this, since a spin coat method can form the thin film of uniform thickness in a short time, it is the especially desirable applying method. A paint film is dried after spreading and a clear layer is obtained by baking at 100 degrees C – 1000 degrees C.
[0024] Generally, since the interface acid-resisting ability between layers in a multilayered film is determined by the refractive index, the thickness, and the number of laminating thin films of a thin film, also in the transparence electric conduction film of this invention, the effective acid-resisting effect is acquired by designing the thickness of each conductive layer and a clear layer in consideration of the number of laminatings of a conductive layer and a clear layer. In the multilayers which have acid-resisting ability, when setting to lambda wavelength of the reflected light which it is going to prevent, if it is the antireflection film of a two-layer configuration, reflection can be effectively prevented by making a high refractive-index layer and a low refractive index into the optical thickness of 4-lambda [lambda/]/4, or lambda/2-lambda/4 from a base material side, respectively. Moreover, if it is the antireflection film of 3 lamination, to consider as the optical thickness of lambda/4-lambda/2-lambda/4 at the order of an inside refractive-index layer, a high refractive-index layer, and a low refractive-index layer will be confirmed from a base material side.
[0025] SiO2 with which the refractive index was comparatively low in the upper layer of a conductive layer and which it combines with rebound ace court nature in it when the ease and economical efficiency on manufacture were especially taken into consideration It is suitable to form a film (refractive index 1.46) by lambda/4 of thickness.
[0026] The transparence electric conduction film of this invention containing a conductive layer and a clear layer may perform printing of a conductive layer and a clear layer one by one, or may perform it to coincidence. For example, by applying the aforementioned coating for conductive layer formation to the screen of a display, applying the coating for clear layer formation to the upper layer, and carrying out package printing after desiccation at the temperature within the limits of 100 degrees C – 1000 degrees C, a conductive layer and a clear layer can be formed in coincidence, and the transparence electric conduction film of low reflexibility can be formed.
[0027] It is desirable to prepare the clear layer which has irregularity in the outermost layer of said transparence electric conduction film. This concavo-convex layer scatters the surface reflected light of a transparence electric conduction film, and is effective in giving the anti-dazzle property excellent in the screen. As the quality of the material of a concavo-convex layer, the viewpoint of surface hardness and a refractive index to a silica is suitable. This concavo-convex layer can apply the coating for concavo-convex stratification with the various aforementioned coating methods as an outermost layer of said transparence electric conduction film, and can bake and form it in a conductive layer, an aforementioned clear layer and aforementioned coincidence, or an exception individual after desiccation at the temperature within the limits of 100 degrees C – 1000 degrees C. Especially as the formation method of a concavo-convex layer, a spray coating method is suitable.
[0028] Even if there are few transparence electric conduction films of this invention, the coloring matter may contain in any one layer. This coloring matter is used for improvement in the contrast of a transparency image, and the color adjustment of the transmitted light and the reflected light. As this coloring matter, for example A monoazo pigment, Quinacridone, iron oxide yellow, A JISUAZO pigment, Phthalocyanine Green, copper phthalocyanine blue, Cyanine blue, flavan SURON yellow, JIAN surra quinolyl red, Indanthrone blue, thioindigo Bordeaux, perylene Orange, Perylene Scarlett, the perylene red 178, perylene MARUN, Dioxazine violet, iso indoline yellow, 2 KKERU nitroso yellow, A MADA lake, copper azomethine yellow, aniline black, alkali blue, A zinc white, titanium oxide, rouge, chrome oxide, iron black, titanellow, cobalt blue, Cerulean blue cobalt green, alumina HOWAITO, kinky thread JIAN, Cadmium yellow, cadmium red, a vermilion, a lithopone, the chrome yellow, a molybdate orange, Zinc chromate, a calcium sulfate, a barium sulfate, a calcium carbonate, the white lead, Organic and inorganic pigments, such as ultramarine blue, manganese violet, emerald green, Berlin blue, and carbon black, And azo dye, anthraquinone dye, indigoid dye, phthalocyanine dye, Colors, such as a carbonium color, a quinonimine dye, methine dye, quinoline dye, nitro dye, nitroso dye, a benzoquinone color, a naphthoquinone color, the North America Free Trade Agreement RUIMIDO color, and a peri non color, can be mentioned. These coloring matters are independent or can be used combining two or more sorts.
[0029] When using a coloring matter, the class and amount should be suitably chosen corresponding to the optical film property of a corresponding transparence electric conduction film. Generally the absorbance A of a transparency thin film is expressed with the following formula.
The inside of an A=log10(I0/I) =epsilonCD type, and I0 For incident light and I, the transmitted light and C are [an optical distance and epsilon of the depth of shade and D] molar extinction coefficients.
[0030] When using a coloring matter by the transparence electric conduction film of this invention, generally the coloring matter of epsilon> 10 is used for a molar extinction coefficient. Moreover, although the loadings of a coloring matter change depending on the molar extinction coefficient of the coloring matter to be used, it is desirable that it is the amount which the absorbance A of the cascade screen which blended the coloring matter, or monolayer becomes within the limits of 0.0004 – 0.0969abs. When these conditions are not fulfilled, transparency and/or the acid-resisting effect fall. When blending the above-mentioned coloring matter with a conductive layer, as for especially the loadings, it is desirable to consider as 10 or less % of the weight 20 or less % of the weight to a metaled content. When 20 % of the weight is exceeded, a conductive fall will be accepted and trouble will be caused to an electromagnetic wave shielding effect.

[0031] As for the display of this invention, it comes to form one of the aforementioned transparence electric conduction films in the screen. Endurance is high even if it is in environment which is put to **** since an image is bright since various kinds of electromagnetic wave disorder is prevented since ** etc. does not adhere to an image display side since, as for this display, electrification of the screen is prevented, but an electromagnetic wave is covered, and it excels in light transmission nature, the hue of a transparency image is natural, the appearance of the screen is good and salt water resistance is moreover high. Moreover, if the aforementioned clear layer and/or the aforementioned concavo-convex layer other than a conductive layer are formed, the outstanding acid-resisting effect and/or the outstanding anti-dazzle effect over outdoor daylight will also be acquired.
[0032]
[Example] Hereafter, this invention is not limited by these examples although an example explains this invention concretely. The following were adjusted as an undiluted solution common to an example and the example of a comparison.
(Hydrosol of golden particle chain-like floc) The aqueous solution of pH5.7 containing the chloroauric acid of 0.15 millimols / liter and the sodium borohydride of 0.15 millimols / liter were mixed, the obtained colloid dispersion liquid were condensed, and the hydrosol containing the chain-like floc of a 0.102 mols [/l.] golder particle was obtained.
(Golden particle independent part water spray nature sol) The aqueous solution of pH3.9 containing the chloroauric acid of 0.15 millimols / liter and the sodium borohydride of 0.50 millimols / liter were mixed, the obtained colloid dispersion liquid were condensed, and the hydrosol containing the 0.102 mols [/l.] golden particle which carried out independent distribution was obtained.
[0033] (Hydrosol of silver particle chain-like floc) The aqueous solution (25g) of pH5.9 which dissolved the silver nitrate (2.5g) in the 5-degree C aqueous solution (60g) which dissolved sodium-citrate dihydrate (14g) and a ferrous sulfate (7.5g) was added, and the dark reddish-brown silver sol was obtained. After rinsing this silver sol according to centrifugal separation and removing impurity ion, the hydrosol which adds pure water and contains the chain-like floc of a 0.185 mols [/l.] silver particle was obtained. The amount of the reducing agent (ferrous sulfate) used here was a 2.1 time mol.
(Independent part water spray nature sol of a silver particle) The aqueous solution (25g) of pH5.9 which dissolved the silver nitrate (2.5g) in the 5-degree C aqueous solution (60g) which dissolved sodium-citrate dihydrate (14g) and a ferrous sulfate (14g) was added, and the dark reddish-brown silver sol was obtained. After rinsing this silver sol according to centrifugal separation and removing impurity ion, the hydrosol which adds pure water and contains the 0.185 mols [/l.] silver particle which carried out independent distribution was obtained. The amount of the reducing agent (ferrous sulfate) used here was a 4 time mol.
[0034] (Colloidal silica) It used gold [by Nippon Chemical Industrial Co., Ltd. / "gold / the silica / 30 /"].
(Coating for clear layer formation) A tetra-ethoxy silane (0.8g), 0.1-N hydrochloric acid (0.8g), and ethyl alcohol (98.4g) were mixed, and it considered as the uniform solution.
(Coating for concavo-convex stratification) A tetra-ethoxy silane (3.0g), 0.1-N hydrochloric acid (10g), and ethyl alcohol (87.0g) were mixed, and it considered as the uniform solution.
[0035] (Example 1)
Preparation of the coating for conductive-layer formation: Stirring mixing of the hydrosol (23g) of the aforementioned golden particle chain-like floc, isopropyl alcohol (10g), and the ethyl alcohol (67g) was carrie out, the obtained mixed liquor was distributed by the ultrasonic disperser (product made from BRANSON ULTRASONICS "SO 2 fire 450"), and the coating for conductive layer formation was prepared. As a result of observation by the transmission electron microscope, in this coating for conductive layer formation, the golden particle with a mean particle diameter of 6nm condensed in the shape of a chain, and the average length of that condensation object was within the limits of 10nm - 80nm.
Membrane formation: The cathode-ray tube of the example 1 which has the transparence electric conduction film of acid resistibility was obtained by the above-mentioned coating for conductive layer formation being used for the screen of the Braun tube, applying a spin coater, applying the aforementioned coating for clear layer formation to this spreading side after desiccation using a spin coater similarly, putting this Braun tube into a dryer, baking for 1 hour, processing at 150 degrees C, and forming a transparence electric conduction film.
[0036] (Example 2)
Preparation of the coating for conductive-layer formation: Stirring mixing was carried out, the hydrosol (23g) of the aforementioned golden particle chain-like floc, isopropyl alcohol (10g), colloidal silica (0.46g), and ethyl alcohol (66.54g) were processed like the example 1, and the coating for conductive layer formation was prepared. SiO2 in a coating / weight ratio of Au was 30/100. As a result of observation by the transmission electron microscope, in this coating for conductive layer formation, the golden particle with a mean particle diameter of 6nm condensed in the shape of a chain, and the average length of that condensation object was within the limits of 10nm - 80nm.
Membrane formation: The cathode-ray tube of the example 2 which processes like an example 1 and has the transparence electric conduction film of acid resistibility was obtained using the above-mentioned coating for conductive layer formation.
[0037] (Example 3)
Preparation of the coating for conductive-layer formation: Stirring mixing was carried out, the hydrosol (16.9g) of the aforementioned golden particle chain-like floc, the hydrosol (1.1g) of the aforementioned silver particle chain-like floc, isopropyl alcohol (10g), colloidal silica (0.36g), and ethyl alcohol (71.64g) were processed like the example 1, and the coating for conductive layer formation was prepared. The weight ratio

of SiO2 / Au/Ag in a coating was 30/6/94. As a result of observation by the transmission electron microscope, in this coating for conductive layer formation, the golden particle with a mean particle diameter of 8nm and the silver granule child condensed in the shape of a chain, and the average length of that condensation object was within the limits of 30nm - 100nm.
Membrane formation: The cathode-ray tube of the example 3 which processes like an example 1 and has the transparence electric conduction film of acid resistibility was obtained using the above-mentioned coating for conductive layer formation.
[0038] Use for the screen of the Braun tube the coating for conductive layer formation used in the example 3, and a spin coater is applied. (Example 4) The aforementioned coating for clear layer formation is similarly applied to this spreading side after desiccation using SUPINKO 1 TA. Furthermore, by spraying the aforementioned coating for concavo-convex stratification by the spray, in order to form a concavo-convex layer, putting this Braun tube into a dryer, carrying out printing **** at 150 degrees C for 1 hour, and forming the transparence electric conduction film of 3 lamination with which the concavo-convex layer was formed in the outermost layer The cathode-ray tube of the example 4 which has the transparence electric conduction film of anti-dazzle property and acid resistibility was obtained.
[0039] (Example 5)
Preparation of the coating for conductive-layer formation: Stirring mixing was carried out, the hydrosol (15.8g) of the aforementioned golden particle chain-like floc, the hydrosol (2.2g) of the aforementioned silver particle chain-like floc, isopropyl alcohol (10g), colloidal silica (0.36g), and ethyl alcohol (71.64g) were processed like the example 1, and the coating for conductive layer formation was prepared. The weight ratio of SiO2 / Au/Ag in a coating was 30/12/88. As a result of observation by the transmission electron microscope, in this coating for conductive layer formation, the golden particle with a mean particle diameter of 10nm and the silver granule child condensed in the shape of a chain, and the average length of that condensation object was within the limits of 80nm - 150nm.
Membrane formation: The cathode-ray tube of the example 5 which processes like an example 1 and has the transparence electric conduction film of acid resistibility was obtained using the above-mentioned coating for conductive layer formation.
[0040] (Example 1 of a comparison)
Preparation of the coating for conductive-layer formation: Stirring mixing was carried out, the independent part water spray nature sol (40g) of the aforementioned silver particle, isopropyl alcohol (10g), and ethyl alcohol (50g) were processed like the example 1, and the coating for conductive layer formation was prepared. As a result of observation by the transmission electron microscope, in this coating for conductive layer formation, the silver particle with a mean particle diameter of 10nm carried out independent distributior at homogeneity, and most condensation objects were not accepted.
Membrane formation: The cathode-ray tube of the example 1 of a comparison which processes like an example 1 and has the transparence electric conduction film of acid resistibility was obtained using the above-mentioned coating for conductive layer formation.
[0041] (Example 2 of a comparison)
Preparation of the coating for conductive-layer formation: Stirring mixing was carried out, the aforementioned golden particle independent part water spray nature sol (50g), isopropyl alcohol (10g), and ethyl alcohol (40g) were processed like the example 1, and the coating for conductive layer formation was prepared. As a result of observation by the transmission electron microscope, in this coating for conductive layer formation, the golden particle with a mean particle diameter of 8nm carried out independent distributior at homogeneity, and most condensation objects were not accepted.
Membrane formation: The cathode-ray tube of the example 2 of a comparison which processes like an example 1 and has the transparence electric conduction film of acid resistibility was obtained using the above-mentioned coating for conductive layer formation.
[0042] (Example 3 of a comparison)
Preparation of the coating for conductive-layer formation: Stirring mixing was carried out, the aforementioned golden particle independent part water spray nature sol (23g), isopropyl alcohol (10g), colloidal silica (0.46g), and ethyl alcohol (66.54g) were processed like the example 1, and the coating for conductive layer formation was prepared. SiO2 in a coating / weight ratio of Au was 30/100. As a result of observation by the transmission electron microscope, in this coating for conductive layer formation, the golden particle with a mean particle diameter of 8nm carried out independent distribution at homogeneity, and most condensation objects were not accepted.
Membrane formation: The cathode-ray tube of the example 3 of a comparison which processes like an example 1 and has the transparence electric conduction film of acid resistibility was obtained using the above-mentioned coating for conductive layer formation.
[0043] (Evaluation measurement) The engine performance of the transparence electric conduction film formed on the cathode-ray tube was measured by following equipment or a following method, and viewing estimated appearance.
Chain structure It checks by :TEM observation. Thickness : It measures by SEM observation. Surface electrical resistance : "RORESUTA AP" (4 terminal method) by Mitsubishi Chemical
Electromagnetic wave electric shielding nature : It calculates by said formula 1 on 0.5MHz criteria. Salt water resistance : 0.5MHz electromagnetic wave shielding effect three days after salt water immersion Scratch trial : Under a 1kg load, by the metal part at the tip of a mechanical pencil, film Grind the surface, a blemish is attached and viewing estimates condition. O; with no blemish **; it gets damaged a little. x; it gets damaged. Permeability : "Automatic Haze Meter H III DP" by Tokyo Denshoku Co., Ltd.

Haze : "Automatic Haze Meter H III DP" by Tokyo Denshoku Co., Ltd.
Gross : adjustable angle glossmeter by Tokyo Denshoku Co., Ltd. "MODEL TC-108D"
60 degrees of incident angles Permeability difference : A Hitachi "U-3500" form recording spectrophotometer is used. The difference of the maximum permeability in a light field and the minimum permeability was searched for. (The rate of transparency becomes a flat more, and the hue of a transparency image becomes clear, so that the maximum-minimum permeability difference in a light field is small.) especially -- 10% or less -- the color of a transparency image -- black -- approaching -- ** ** -- it comes to have advanced clearness.
Luminous reflectance Product made from :EG&G GAMMASCIENTIFIC "MODEL C-11"
Reflected color : "CR-300" by Minolta Camera Co., Ltd.
(White point [in / a CIE color coordinate system is used and / a CIE chromaticity diagram] deltax and delta y are used for the distance of gap from x=0.3137 and y=0.3198 . root (deltax2 +deltay2))
It came out and expressed. thereby -- the value of root (deltax2 +deltay2) -- more -- The thing nearer to "0" has a reflected color kinder to white, i.e., an eye. It becomes a thing near the natural light.
Visibility : The comprehensive evaluation containing the low reflective engine performance, a reflected color, and a transparency color O ; [Fitness] A little **; O Fitness, ** ; Good A little **x; A defect x ; defect Film nonuniformity : Homogeneous evaluation of the appearance color by viewing O ; Good O**; -- a little -- fitness ** ; good **x; -- a little -- defect x ; The evaluation test result beyond a defect is shown in a table 1 and a table 2.
[0044]
[A table 1]

	連鎖状凝集体の平均長さ (nm)	膜厚 (nm)	表面抵抗 (Ω／□)	0.5MHz 電磁波遮蔽性(dB)	耐塩水性(dB)	ｽｸﾗｯﾁ試験	透過率 (%)
実施例1	10～80	25	4×10^2	83	83	△	85.0
実施例2	10～80	25	5×10^2	82	82	○	86.1
実施例3	30～100	20	3×10^2	84	84	○	88.2
実施例4	30～100	20	4×10^2	83	83	○	89.0
実施例5	80～150	25	3×10^2	84	84	○	83.5
比較例1	／	40	2×10^2	84	17	△	60.7
比較例2	／	55	1×10^4	66	66	×	66.0
比較例3	／	35	4×10^3	72	72	△	78.5

[A table 2]

	ﾍｲｽﾞ (%)	ﾀﾞｽ (%)	透過率差 (%)	視感反射率 (%)	反射色 ($\sqrt{(\Delta X^2+\Delta Y^2)}$)	視認性	膜ムラ
実施例1	0.2	103.2	5	0.95	0.010	○△	○
実施例2	0.1	101.2	4	0.91	0.020	○△	○
実施例3	0.0	100.5	3	0.90	0.003	○	○
実施例4	1.2	77.2	4	0.72	0.005	○	○
実施例5	0.4	100.5	6	0.95	0.010	○△	○
比較例1	0.0	101.9	27	0.58	0.120	×	△
比較例2	0.2	101.4	11	0.92	0.030	△	○△
比較例3	1.0	100.2	6	1.50	0.003	×	○

[0045] The cathode-ray tube of this invention with which the transparence electric conduction film containing the chain-like floc of a metal particle was formed from the result of the above-mentioned table 1 and a table 2 It compares with the example 1 of a comparison which contains in the conventional homogeneity the metal particle which carried out independent distribution, the example 2 of a comparison, and the example 3 of a comparison. Although thickness is 1/2 or less thinness, surface electrical resistance and electromagnetic wave electric shielding nature are an EQC - more than an EQC. It excels also in salt water resistance and scratch-proof nature, especially permeability is excellent, transparency is high, moreover, since the permeability difference is small, the hue of a transparency image is not spoiled, but there is little reflection and a reflected color is also understood that there is little coloring and visibility and film nonuniformity are also good. It turns out that as for the example 4 a gross decreases since the concavo-convex layer is formed in the outermost layer, a reflect lump of outdoor daylight is controlled, and

the transparency image has become still more legible.
[0046]
[Effect of the Invention] Since the transparence electric-conduction film of this invention has the conductive layer formed by applying the coating for conductive layer formation which the chain-like floc of a metal particle distributed, the formed transparence electric conduction film has good conductivity, its light average transmission coefficient is high, when it excels in an electromagnetic wave shielding effect and the antistatic effect and the chain-like floc of a golden particle is used especially, the hue of a transparency image is natural, and it excels also in the endurance moreover represented by salt water resistance. Therefore, the hue of a transparency image is not spoiled, but the display of this invention with which this transparence electric conduction film was formed in the screen has the outstanding antistatic nature and electromagnetic wave electric shielding nature, and chemical stability, moreover, since light transmission nature is high, a transparency image is bright and the thickness nonuniformity of a paint film is not conspicuous, either.

[Translation done.]

* NOTICES *

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The mimetic diagram showing the gestalt of the chain-like floc of a metal particle
[Description of Notations]
(1) The shape of a straight chain
(2) Branched-chain
(3) Annular
(4) Compound gestalt

[Translation done.]